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Conversion Dependence of the Branching Density for the Polycondensation of AB_n Monomers

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ABSTRACT: The distribution function of differently branched molecules resulting from the ideal statistic condensation of AB_2 functional monomers is calculated as a function of the conversion of the A groups. For these distribution functions the averaged branching parameters DB_F = (number of terminal groups + number of dendritic groups)/degree of polymerization and DB_{HF} = number of dendritic groups/maximum number of dendritic groups are calculated. In the more general case of AB_n polycondensates, equations are given to calculate the weight fraction of branched units directly from the degree of A-group conversion. Additionally, expressions for the polycondensations kinetics are derived, yielding the conversion and the degree of polymerization as a function of time.

Introduction

"Dendrimers" are maximum branched polymers with a extremely small polydispersity. These well-defined molecules are of particular interest for the utilization in catalysis, supramolecular chemistry, and biochemistry, where the structural definitions are of great importance. They also provide valuable model compounds for the investigation of structure−property relationships in polymer materials. However, because of the high costs of dendrimers, caused by their cumbersome preparation, it is still questionable if they can ever be used for large scale practical applications.[1−6]

In most material applications "hyperbranched" polymers do show properties very similar to dendrimers, but their syntheses are accomplished by simple one-pot polycondensations of multifunctional monomers.[7] Hyperbranched polymers do not possess such regular structures as dendrimers and normally their polydispersities are rather high. There are attempts to maximize branching by suitable control of the chemical reactions. Therefore there is a need to describe the degrees of branching and the molecular weight distributions of hyperbranched products as a function of conversion and reactivity.

For the most part synthesis of hyperbranched polymers is done by the self-condensation of AB_n monomers, principally avoiding the formation of infinite large network structures.[7] The theoretical description of polycondensations leading to branched products was first done by Stockmeyer[8−10] and Flory;[11] further investigations on this subject came from Gordon[12−17] and Burchard.[18−20] Flory derived the molecular weight distribution and gave expressions for the characteristic mean values such as M_n, M_w and M_w/M_n of AB_n polymers.[11] Most theoretical considerations are based on the assumptions that no intermolecular ring formation will occur and that sterical effects will be negligible, stating that all functional groups are of the same reactivity. Flory did not investigate the distribution of the branching units over the molecules or give a satisfactory definition for a "degree of branching" for hyperbranched polymers.

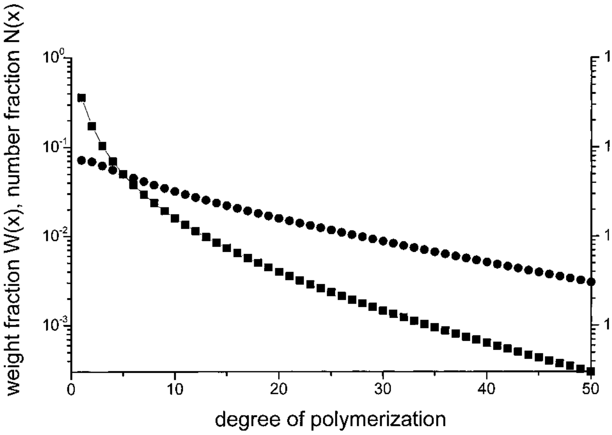

Figure 1. Theoretical molecular weight distribution of an AB_2 polycondensation product at a degree of B-group conversion $p_B = 0.4$ [9]: (■) number fraction $N(x)$; (●) weight fraction $W(x)$

This study gives a description of the distribution of branching units for AB_2 polycondensates dependent on the conversion of the A groups and the conversion as a function of time for the polycondensation of AB_n monomers.

Result and Discussion

(A) Branching as a Function of Conversion. In the case of the polycondensation of an AB_n monomer, Flory derived for a given degree of conversion of the B groups p_B that the molecular weight distribution is given by the following expressions:[11]

$$N(x) = \frac{1 - p_B}{p_B}\omega(x)(p_B(1 - np_B))^x \tag{1}$$

$$W(x) = \frac{1 - p_B}{p_B}(1 - np_B)\omega(x)(p_B(1 - np_B))^x \tag{2}$$

$$\omega(x) = \frac{(2x)!}{(x + 1)!x!} \tag{3}$$

In this series of equations n is the ratio of B:A groups, $N(x)$ denominates the molar (=number) fraction of an x-mer with the degree of polymerization x, $W(x)$ belongs to the weight fraction, and $\omega(x)$ gives the number of isomeric structures, which can be formed by xAB_n monomers.

This distribution is visualized in Figure 1 for $n = 2$ and $p_A = 0.8$, depicting N(x) and W(x) as functions of

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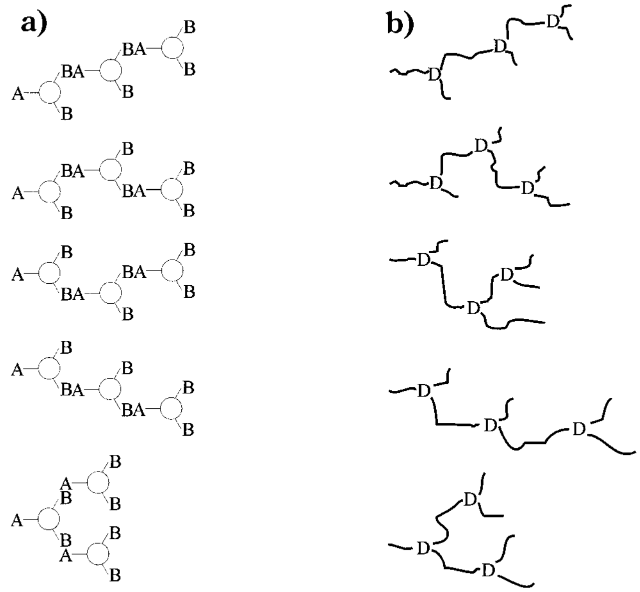

Figure 2. Schematic sketch illustrating the identical number of isomers arising from the combination of three AB_2 monomers or three dendritic units D.

the degree of polymerization x. In contrast to the weight distribution of linear AB polycondensation products, W(x) decreases continuously with increasing x. This shows that unreacted AB_n monomer always will affect the properties of the branched product.

To gain more precise information about the distribution of the branching units d, the total number of possible isomers, $\omega(x,d)$, with a given degree of polymerization x and a given number of branching units d has to be calculated. If cyclization is neglected and equal reactivity of each functional group is considered, $\omega(x,d)$ can be calculated for the AB_2 case in the following way:

$$\omega(x,d) = \omega(d)\omega(dl)\omega(l) \tag{4}$$

Herein $\omega(d)$ is the number of ways in which d branching units can mutually be arranged, forming a "dendritic framework". $\omega(dl)$ is the number of possibilities of place l linear groups inside the dendritic framework, and $\omega(l)$ gives the number of different structures arising from sequences of l linear arranged AB_2 units.

Since in the AB_2 system the functionality of every branching unit is identical to the functionality of the monomer itself, $\omega(d)$ has to be identical, with the total numbers of isomers to be formed by dAB_2 molecules: $\omega(d) = (2d)!/[(d + 1)!\, d!]$, cf. eq 3 and Figure 2.

A branching unit offers two possibilities to add a subsequent unit, while a linear unit gives only one. Consequently, in the dendritic framework $2d + l$ places can be filled with l linear structure units. The problem of finding $\omega(dl)$ is therefore reduced to finding the number of possibilities to distribute l linear units over $2d + l$ positions. This standard question of combinatorics is solved by[21]

$$\omega(dl) = \binom{2d + l}{l} = \frac{(2d + l)!}{(2d)!\,l!} \tag{5}$$

If l AB_2 units are arranged in a linear chain, 2^l different chains are possible. Since this number is not affected if branching units are incorporated in the sequence, $\omega(l)$ is given as

$$\omega(l) = 2^l \tag{6}$$

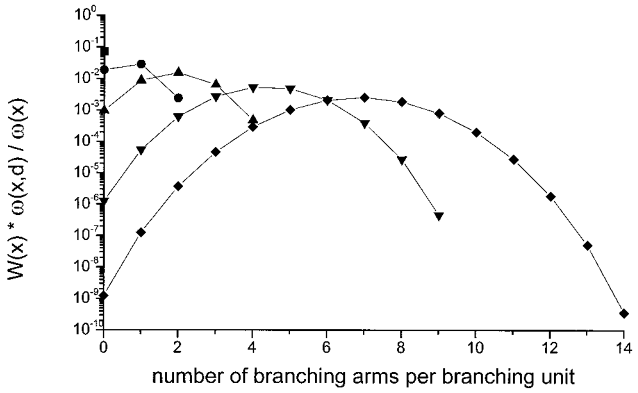

Figure 3. Theoretical weight distribution of the number of branching units d for different degrees of polymerization x at a degree of B-group conversion $p_B = 0.4$: (■) $x = 1$; (●) $x = 5$; (▲) $x = 10$; (▼) $x = 20$; (◆) $x = 30$.

In hyperbranched AB_2 x-mers it can be shown that the number of terminal groups is $t = d + 1$ and the number of linear groups depends on the degree of polymerization and the number of branching units:

$$l = x - 1 - 2d \tag{7}$$

Combination of eqs 4–7 let us find the wanted number of isomeric x-mers with a given number of branching units d:

$$\omega(x,d) = \omega(d)\frac{(x - 1)!}{(x - 1 - 2d)!(2d)!}2^{x-1-2d} \tag{8}$$

The total number of x-mers is obtained by summation over all structures with different numbers of branching units, possible for a given degree of polymerization x. The highest possible number of maximal branched units is easily calculated, if in eq 7, l, the number of linear units, is set at zero. Note that one has to distinguish between odd and even degrees of polymerization.

$$d_{\max}(x) = \begin{cases} \dfrac{x - 2}{2}, & x = 2k \\ \dfrac{x - 1}{2}, & x = 2k + 1 \end{cases} \tag{9}$$

By combination of eqs 3, 8, and 9, one obtains the normalization condition for the distribution of branched units:

$$\sum_{d=0}^{d_{\max}} \frac{\omega(x,d)}{\omega(x)} = 1 \tag{10}$$

Figure 3 depicts the calculated weight fraction $W(x,d) = W(x)\omega(x,d)/\omega(x)$ for different degrees of polymerization x at a B group conversion of 40%. As is to be expected, the weight fraction of linear isomers $W(x,0)$ as well as the weight fraction of the pure dendritic structures $W(x,d_{\max}(x))$ decreases rapidly with the increasing degree of polymerization. This clearly demonstrates that high degrees of branching can never be established via polycondensation of AB_2 polymers. From Figure 3, it can be seen that the main contribution always arises from the isomers containing $d = d_{\max}(x)/2$ branching units.

The distribution can experimentally be determined by careful fractionation of AB_n polymers to obtain

Table 1. Definitions for Different Degrees of Branching[a]

eq 11	"coefficient of branching"	$\alpha = p_B = p_A/n$	Flory[11]
eq 12	"degree of branching"	$DB_F = (\sum t + \sum d)/(\sum t + \sum d + \sum l)$	Frechet[22]
eq 13	"degree of branching"	$DB_{HF} = d/d_{max}$	Frey[23]

[a] Key: t = number of terminal units, d = number of branching units, and l = number of linear units, each per molecule respectively.

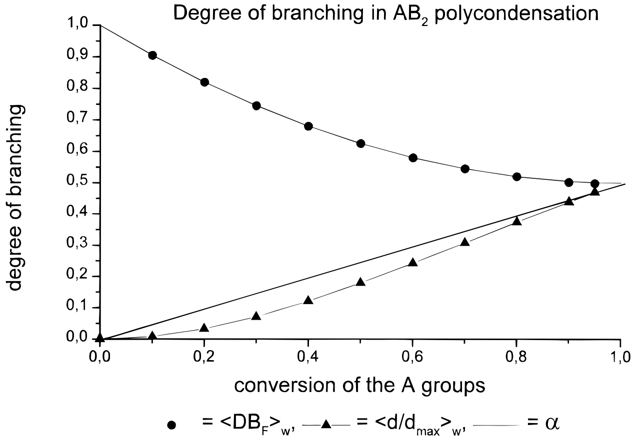

Figure 4. Comparison of the conversion dependance for different "degrees of branching" applied to the theoretical weight distribution of a hyperbranched AB$_2$ polycondensation product: (●) Frechet parameter; (▲) Hölter–Frey parameter; (—) Flory parameter.

fractions with a definite degree of polymerization. Subsequently, by combination of NMR techniques[22,23,26] or HPLC/MALDI-TOF[25] the distribution of linear and dendritic groups should be measurable.

To get a characteristic value describing the extent of branching in a polymeric product, several parameters were proposed (cf. Table 1).

The "coefficient of branching" (α, cf. eq 11 in Table 1), proposed by Flory gives "the probability, that a given functional group of a branch unit leads ... to another branch unit". In the case of AB$_n$ polycondensation it was shown that α is identical to the conversion of the B groups.[11] This means that no information can be extracted about the extent of branching from α, since every reacted B group can either be part of a linear or a branched unit.

Frechet[22] and Frey[23] used branching parameters, defined to describe the extend of branching in monodisperse dendritic or hyperbranched polymers (cf. eqs 11 and 12 in Table 1). To apply these concepts to the statistical AB$_2$ polycondensation, first the degree of branching has to be averaged over all isomers with a constant degree of polymerization and second the average over the whole distribution of the molecular weights has to be calculated. If one remembers that in AB$_2$ x-mers the number of terminal groups is $t = d + 1$, the weight average of the Frechet parameter DB$_F$ and the Hölter–Frey parameter DB$_{HF}$ can be expressed as

$$\langle DB_F \rangle_w = \sum_{x=1}^{\infty} W(x) \sum_{d=0}^{d_{max}} \frac{\omega(x,d)}{\omega(x)} \frac{2d+1}{x} \tag{14}$$

$$\langle DB_{HF} \rangle_w = \sum_{x=1}^{\infty} W(x) \sum_{d=0}^{d_{max}} \frac{\omega(x,d)}{\omega(x)} \frac{d}{d_{max}(x)} \tag{15}$$

In Figure 4 the numerically calculated values of $\langle DB_F \rangle_w$ and $\langle DB_{HF} \rangle_w$ are plotted vs the conversion of the A groups. It can be seen that $\langle DB_F \rangle_w$ decreases from 1.0 ($p_A = 0$) to 0.5 at full conversion. This behavior occurs because the DB$_F$ of the monomer always has the value 1.0 and so the monomer content in the molecular weight distribution prevents $\langle DB_F \rangle_w$ from decreaseing to below 0.5. A value of $\langle DB_F \rangle_w$ smaller than 0.5 can only be obtained by removing the unreacted monomer from the polycondensation product.

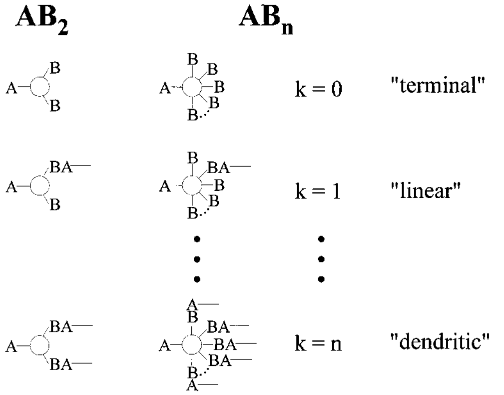

Figure 5. Schematic sketch showing the meaning of "terminal", "linear", and "dendritic" units in AB$_2$ and AB$_n$ polycondensation products.

In contrast to this, the Hölter–Frey parameter increases with increasing conversion from zero ($p_A = 0$) to 0.5. The Flory parameter, not containing any branching information, linearly increases up to a value of 0.5. From these results, the Hölter–Frey parameter seems to give the best measurement of branching in a polydisperse hyperbranched AB$_2$ polycondensate, since one expects an increase in branching if more and more molecules add to a given branched structure.

The Frechet parameter can be calculated without evaluating the summations of eq 14. In an AB$_2$ x-mer, only three types of structures (linear, dendritic, and terminal units; cf. Figure 5) can occur. The probability for the occurrence of each structure (P(L), P(D), and P(T)) can be calculated from the reaction probability of the B groups p_B (eqs 16–18).

$$P(D) = p_B^{\,2} \tag{16}$$

$$P(L) = 2p_B(1 - p_B) \tag{17}$$

$$P(D) + P(L) + P(T) = 1 \tag{18}$$

If one assumes, that the content of a structure unit in an polymer sample is proportional to the probability for building this structure unit, the following equations are obtained:

$$\langle DB_F \rangle_w = \frac{P(D) + P(T)}{P(D) + P(T) + P(L)} \tag{19}$$

$$\langle DB_F \rangle_w = 1 - 2p_B + 2p_B^{\,2} \tag{20}$$

It can be shown that in polydisperse polymer samples the weight average of DB$_F$ is calculated, since every molecule contributes with all its structural units, their number being identical to the degree of polymerization.

Table 2. Limiting Value of $\langle DB_F\rangle_w$ for Total Conversion of the A Groups in an AB_n Polycondensation

n	$\langle DB_F\rangle_w(p_B = 1/n)$	n	$\langle DB_F\rangle_w(p_B = 1/n)$
2	0.5000	5	0.3280
3	0.3333	6	0.3349
4	0.3203	∞	0.3679

In the general case of an AB_n system, the probability of finding a unit with k −AB− connections (cf. Figure 4) can be evaluated:

$$\langle P_k^{\ n}\rangle_w = \binom{n}{k} p_B^{\ k}(1 - p_B)^{n-k} \tag{21}$$

Using eq 18, the weight average of the Frechet parameter can be calculated if we take $P(T) = P(n,0)$ and $P(D) = P(n,n)$.

$$\langle DB_F\rangle_w = (1 - p_B)^n + p_B^{\ n} \tag{22}$$

Since the degree of conversion of the B groups (p_B) in the case of complete conversion of all A groups cannot exceed $1/n$, the limiting value of $\langle DB_F\rangle_w$ will be

$$\lim_{p_B \to 1/n} \langle DB_F\rangle_w = \left(1 - \frac{1}{n}\right)^n + \frac{1}{n^n} \tag{23}$$

It is instructive to calculate this limiting value for several values of n (cf. Table 2). Above $n = 4$, $\langle DB_F\rangle_w$ ($p_B = 1/n$) increases with increasing n. In the limiting case $n \to \infty$, $\langle DB_F\rangle_w$ ($p_{AB} = 1/n$) becomes equal to $1/e = 0.3679$. The increase of $\langle DB_F\rangle_w$ ($p_B = 1/n$) is caused by the extremely fast growth of the number of terminal groups, overcoming all other contributions of linear or branched units. Since the Frechet parameter was developed for monodisperse AB_2 dendrimers, it cannot expected to be useful in the general case of a AB_n polycondensation.

In general it seems doubtful if only one parameter would be able to give a good characterization of a broadly distributed hyperbranched polymer. Perhaps, it would be more convenient to use eq 21 to calculate the weight averages of the structure units of interest and compare them to the experimentally observed values.

(B) Conversion as a Function of Time. Except from *Hult*,[24] who investigated the polycondensation of a special type of AB_2 monomer, to our knowledge, no one has reported kinetic equations describing the degree of conversion and the degree of polymerization as a function of reaction time in the polymerization of AB_n monomers. To do this, we will use the following assumptions:

The reaction is bimolecular and A groups can only react with B groups:

$$A + B \xrightarrow{k_n} AB$$

The reactivity of all groups is identical, so the overall reaction velocity is fully determined by one velocity constant.

No sterical hindrance will occur; the velocity constant will not depend on the degree of polymerization or the branching structure of the macromolecule.

No cyclization will occur; a single molecule can grow without limitations.

The reaction is not catalyzed by one of the functional groups A or B.

It is still clear that some of these assumptions may hold only up to low degrees of conversion, but the derived expressions will still be useful to determine the point where these assumptions are no longer valid.

Usually the kinetics of a polycondensation (or polyaddition) can be directly derived from the organic reaction on which it is based. Since a bimolecular reaction between the two functional groups A and B is assumed, the velocity law is

$$\frac{dx}{dt} = k_n([A]_0 - x)([B]_0 - x) \tag{24}$$

In this equation $[A]_0$ and $[B]_0$ are the starting concentrations of the functional groups, x is the concentration of built −AB− links and k_n denominates the velocity constant. If a catalyst is present its concentration will remain constant and can be included into k_n: $k_n = [\text{catalyst}]k_n^*$. In an AB_n monomer, the concentrations of the functional groups are connected to the monomer concentration: $[B]_0/n = [A]_0 = [M]_0$. Dividing eq 24 by $1/[M]_0^2$, taking into account that $[A]_0/[M]_0 = 1$ and $[B]_0/[M]_0 = n$ and introducing the conversion parameter $\lambda = x/[M]_0$, the equation is simplified to

$$\frac{1}{[M]_0}\frac{d\lambda}{dt} = k(1 - \lambda)(n - \lambda) \tag{25}$$

The integration of this differential equation can be found in the literature,[19] and for $n > 1$ one finds:

$$\ln\left|n\frac{\lambda - 1}{\lambda - n}\right| = (1 - n)k_n[M]_0 t \tag{26}$$

Equation 26 is useful for the evaluation of kinetic measurement data. A deviation from the linear behavior, suggested by eq 26, would directly show the occurrence of deviations from the idealized reaction kinetics. Rearranging to isolate λ yields:

$$\lambda = p_A = \frac{1 - e^{(1-n)k_n[M]_0 t}}{1 - \frac{1}{n}e^{(1-n)k_n[M]_0 t}} \tag{27}$$

Since λ can be identified as the degree of conversion of the A groups, the number average of the degree of polymerization $\langle x\rangle_n$ can be expressed in a time-dependent way:

$$\langle x\rangle_n = \frac{1}{1 - \lambda} = \frac{n - e^{(1-n)k_n[M]_0 t}}{(n - 1)e^{(1-n)k_n[M]_0 t}} \tag{28}$$

In Figure 6a, the degree of conversion p_A is plotted vs the time-dependent parameter $[M]_0 k_n t$ for the AB and the AB_2 case; in Figure 6b, the time dependence of the degree of polymerization is shown. Due to the fact that the ratio of B:A groups in an AB_n monomer increases with n, the reaction proceeds much faster than in the case of the linear AB polycondensation.

Conclusion

The present work gives an idealized picture of the growth and the structure of AB_n polymers neglecting sterical influences. Comparison with experimental data will allow us to measure the degree of A-group conversion at which the sterical overcrowding becomes the dominating factor, determing the overall shape of the AB_n polycondensate.

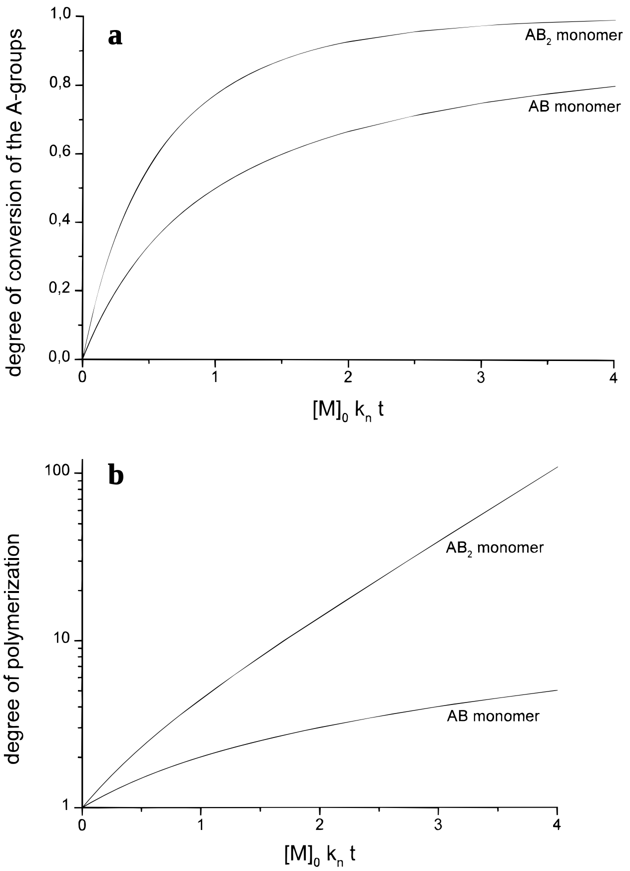

Figure 6. Theoretical calculation of the time dependence of (a) the conversion of A groups and (b) the degree of polymerization for a linear AB polycondensation and a branched AB_2 polycondensation.

By expansion of Florys theory of AB_n polycondensation, the distribution of molecules containing arbitrary numbers of branching units was derived.

In the case of an ideal statistically polycondensation of AB_n monomers, the weight fraction of every branching unit in the polymeric product can easily be calculated and compared to experimental results. Monomer rigidity and finite monomer volumn will affect the point at which the real systems deviate from the stochastic description in this work.

These parameters, derived for the description of unidisperse or low dispersing polymeric systems, should only be used in combination with a detailed description of the investigated system. It seems to be more convenient to communicate all the contents of $-AB-$, $-AB_2-$, ..., $-AB_{n-1}$ branching units, instead of hiding them by coding into a single number.

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